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1. Title of the Invention

Method for Purifying Terephthalic Acid

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5. Attachments

(1) Specification	1 copy
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(3) Power of Attorney	1 copy

SPECIFICATION

1. Title of the Invention

Method for Purifying Terephthalic Acid

2. Claims

A method for purifying crude terephthalic acid obtained as a result of subjecting *p*-dialkylbenzene to an oxidation reaction in a liquid phase in the presence of a cobalt compound, with a gas containing molecular oxygen being blown thereinto, said method for purifying terephthalic acid characterized in that a suspension of the terephthalic acid is first prepared in such a manner that an aqueous solution of acetic acid containing 5 to 40 wt% of water is present in an amount 2 to 10 times as large in terms of the weight of the dried crude terephthalic acid; the temperature of the suspension is brought to between 40 and less than 140°C; the terephthalic acid is thereby washed with the aqueous solution of acetic acid; the terephthalic acid is subsequently separated; a suspension of the terephthalic acid is again prepared so that an aqueous solution of acetic acid containing 5 to 40 wt% of water is present in an amount 2 to 10 times as large in terms of the weight of the dried terephthalic acid; the temperature of the suspension is adjusted to between 140 and less than 180°C; and the terephthalic acid is thereby washed with the aqueous solution of acetic acid.

3. Detailed Description of the Invention

The present invention relates to an improved method for washing slurries of crude terephthalic acid obtained as a result of subjecting *p*-dialkylbenzene to low-temperature liquid-phase oxidation using molecular oxygen; and particularly relates to a method for manufacturing high-purity terephthalic acid that can be used in the so-called direct method, wherein polyethylene terephthalate is obtained by means of reacting and polymerizing terephthalic acid directly with ethylene glycol or ethylene oxide without the use of a dialkyl ester of terephthalic acid.

A variety of oxidation treatments, reduction treatments, recrystallization, sublimation treatments, combinations thereof, and other methods have been proposed as techniques for

improving the purity of crude terephthalic acid. The so-called slurry method is known for treating crude terephthalic acid in a variety of solvents in a suspended state.

Subjecting *p*-xylene to low-temperature liquid-phase air-oxidation is a typical method for manufacturing terephthalic acid. A variety of impurities are contained in crude terephthalic acid obtained as a result of air oxidation. Examples of typical impurities include benzoic acid, *p*-toluic acid, 4-carboxybenzaldehyde, colored matter, and inorganic substances. If crude terephthalic acid that contains such impurities is reacted with ethylene oxide or ethylene glycol, so-called fiber-grade polyethylene terephthalate will not be obtained. One method for purifying terephthalic acid currently used to obtain fiber-grade polyethylene terephthalate involves completely dissolving the terephthalic acid in a suitable solvent and subjecting the resulting product to an oxidation treatment or reduction treatment in solution.

However, no good solvent actually exists for use with terephthalic acid; therefore, terephthalic acid is often either formed into an alkali solution or treated as a solution under high temperature and high pressure. It is clear that in the former case, complicated processes are required to recover the alkali, while in the latter case the equipment used creates economic disadvantages.

On the other hand, many improved slurry washing methods have been proposed, as has been described above. At present, all of these methods are only valuable as preliminary pretreatments for obtaining high purity terephthalic acid from crude terephthalic acid. For this reason, it is extremely difficult to manufacture fiber-grade polyethylene terephthalate by means of reacting and polymerizing crude terephthalic acid directly with ethylene glycol or ethylene oxide merely by way of conventional slurry washing.

When *p*-alkylbenzene, in particular, is subjected to air oxidation, an expensive cobalt compound is used as the catalyst. Consequently, with conventional slurry washing, where purifying the crude terephthalic acid is the only objective, recovery and reuse have been virtually impossible without a loss of activity.

If the expensive catalysts used in low-temperature liquid-phase air oxidation could be recovered and reused solely by means of slurry washing, and if it were possible to simultaneously

obtain essentially the same level of effect as obtained in solution in the previously described treatment, considerable economic advantage could be realized in view of the facts that lower quantities of catalyst and solvent would be used, no alkali or acid would be used, and high temperatures and high pressures would not be used.

It is an object of the present invention to provide a method for commercially and inexpensively manufacturing high-purity terephthalic acid by means of purifying crude terephthalic acid obtained as a result of a method in which expensive cobalt is recovered from the low-temperature liquid-phase air oxidation reaction products without any loss in catalytic activity, and by means of the oxidation that occurs at the same time.

It is a further object of this invention to provide an improved slurry washing method for manufacturing high-purity terephthalic acid suitable for the direct polyester polymerization of crude terephthalic acid.

The present inventors carried out investigations, and unexpectedly ascertained as a result thereof that the two objectives of the present invention as stated in the foregoing could be simultaneously achieved as a result of performing a treatment using a specified solvent composition and under specified conditions. This was contrary to the hitherto prevailing view that high-purity terephthalic acid of a similar level to that obtained with dissolution treatments could probably not be manufactured by means of combining slurry washing with the recovery and reuse of cobalt compounds having extremely high activity in the air oxidation of *p*-dialkylbenzene from the reaction products.

In other words, when crude terephthalic acid is obtained as a result of subjecting *p*-dialkylbenzene to an oxidation reaction in a liquid phase in the presence of a cobalt compound, with a gas containing molecular oxygen being blown thereinto, a means is adopted wherein a suspension of the terephthalic acid is first prepared in such a manner that an aqueous solution of acetic acid containing 5 to 40 wt% of water is present in an amount 2 to 10 times as large in terms of the weight of the dried crude terephthalic acid; the temperature of the suspension is brought to between 40 and less than 140°C; the terephthalic acid is thereby washed with the aqueous solution of acetic acid; the terephthalic acid is subsequently separated; a suspension of the terephthalic acid is again prepared so that an aqueous solution of acetic acid containing 5 to

40 wt% of water is present in an amount 2 to 10 times as large in terms of the weight of the dried terephthalic acid; the temperature of the suspension is adjusted to between 140 and less than 180°C; and the terephthalic acid is thereby washed with the aqueous solution of acetic acid. The present invention was achieved based on the discovery that adopting the above means allows the cobalt catalyst used in the reaction to be recovered from the low-temperature liquid-phase oxidation reaction product of *p*-dialkylbenzene without causing a decrease in catalyst activity, unlike when ordinary high-temperature washing is performed; and that the crude terephthalic acid could be efficiently purified. An economical method is accordingly provided for manufacturing high-purity terephthalic acid that can be used to prepare *p*-dialkylbenzene directly by means of a low-temperature liquid-phase air oxidation, which is a highly significant achievement from a commercial standpoint.

The present invention shall be described in further detail hereunder. The term "slurry washing" in the present invention refers to the fact that crude terephthalic acid and hydrated acetic acid are brought into contact in a state wherein the terephthalic acid particles are suspended using acetic acid having a water content of 5 to 40 wt%, after which the terephthalic acid and the contact solution (wash mother liquor) are separated from the suspension. The contacting method may involve stirring the suspension in a tank or tube, or bringing the terephthalic acid and the hydrated acetic acid into contact in a state wherein the terephthalic acid floats in a column. In addition, any method including precipitation, filtration, cycloning, and centrifugation can be used to separate the terephthalic acid and wash mother liquor. However, the centrifugation is preferable from a commercial standpoint. A water content ratio in the acetic acid solution in a range of 5 to 40 wt% during the first slurry wash results in a higher impurity removal efficiency in the crude terephthalic acid, with lower efficiency removal occurring at water content ratios outside this range. The washing temperature is another important factor. Cobalt compounds recovered at 40 to 140°C have an extremely high oxidation catalyst action. By contrast, cobalt compounds obtained once the wash solution obtained by means of separating the terephthalic acid has evaporated after the first slurry washing has been performed at a temperature of 140°C or higher will lose their activity as an oxidation catalyst. It is impossible to obtain uncolored high-purity terephthalic acid if the first slurry wash is performed at a

temperature of 140°C or higher, regardless of how vigorously the second and subsequent slurry washings are performed.

As is known in slurry washing procedures, the first stage slurry washing is performed at a comparatively high temperature. Therefore, fiber-grade terephthalic acid cannot be manufactured economically without the expensive cobalt compound losing its catalytic effect.

Conventionally, the opinion that simple slurry washing should be performed before high-temperature slurry washing is performed has been presented on numerous occasions in the literature. However, as a result of intensive studies, the present inventors unexpectedly ascertained it to be extremely important for preliminary slurring washing to be performed before high-temperature slurry washing, which has generally been thought as common practice.

This suggests that it is absolutely impossible to achieve the objectives of the present invention merely as a result of mechanically combining conventional slurry washing processes. In other words, the conditions of the first slurry washing used in common practice are extremely important, and are an indispensable necessity not only for increasing the effect in the second stage and subsequent slurry washings, but also in terms of commercially manufacturing high-purity terephthalic acid from *p*-dialkylbenzene by means of a low-temperature air oxidation. Nevertheless, the first washing is preferably performed at a temperature of 80 to 120°C.

The water content ratio in the acetic acid solution of the second slurry washing should be 5 to 40 wt%, as in the first washing. A washing temperature of 140 to 180°C is desirable for manufacturing fiber-grade high-purity terephthalic acid. If the temperature is less than 140°C, the removal ratio of the impurities in the crude terephthalic acid will decrease sharply, and no slurry washing effect will be apparent. If the temperature exceeds 180°C, contamination of the terephthalic acid due to corrosion of the apparatus and thermal decomposition of the impurities in the crude terephthalic acid will cause coloration of the terephthalic acid. It is similarly impractical for economic reasons for the temperature to exceed 180°C, since the evaporation pressure of the solvent will abnormally increase, expensive materials will be required, and the method used to remove the terephthalic acid after slurry washing will become complicated. In other words, the solubility of the terephthalic acid increase, and accordingly slurry washing at

temperatures exceeding 180°C will result in the complete dissolution of the terephthalic acid under high temperature and high pressure. The results will be similar to those obtained with recrystallization, and the advantages of slurry washing will accordingly be lost.

Passing from the first to the second slurry washing, the quantity of acetic acid solution used relative to the terephthalic acid should be two to ten times the amount, and preferably four to six times the amount, expressed in terms of parts by weight. If the quantity of solvent used is less than two times as great in terms of in terms of parts by weight, the washing effect will be poor, and slurry movement will be impaired. On the other hand, if more than ten times the amount is used in terms of parts by weight, the quantity of solvent used will be close to that in the recrystallization purification method and a large quantity of acetic acid solution will need to be evaporated off from the final wash, although the slurry washing effect will be somewhat heightened. Such ranges are accordingly uneconomical. There are no particular limitations as to the duration of the first low-temperature slurry wash, but a time of 0.5 to 2 hours is desirable. On the other hand, if the duration of the second high-temperature slurry wash is less than 30 minutes, the washing effect will be extremely low. Conversely, if the process lasts longer than four hours, the impurity content will tend to increase slightly. A time of one to three hours is accordingly desirable.

This invention consists of a first low-temperature (40 to 140°C) slurry wash and a second high-temperature (140 to 180°C) slurry wash. It is possible for the objectives of this invention to be substantially achieved as a result of using these two slurry washes. Nevertheless, it is desirable to utilize a low-temperature slurry wash after the second high-temperature slurry wash because this will achieve the effect of replacing the washing solution attached to the terephthalic acid.

During implementation of the present invention, the atmosphere of the slurry washing system may be an inert gas (for example, carbon dioxide gas or nitrogen) or molecular oxygen (provided that the concentration is at the explosion limit).

The present invention can be performed either by means of a batch or continuous method, and may also be performed with the help of a tank or column method.

The slurry wash of the present invention is suited to crude terephthalic acid that has been obtained as a result of oxidizing *p*-dialkylbenzene by means of known liquid-phase air oxidation methods. Examples of such methods include performing oxidation in the presence of a heavy metal and the optional presence of a bromine compound, or performing oxidation in the presence of a heavy metal, paraldehyde, ketone, or acetaldehyde.

The present invention shall be described in detail below with reference to working examples. In the working examples, "parts" and "%" are in all cases based on a weight standard. Further, the numerical values which express the catalytic activity of the recovered cobalt shown in the working examples (recovered cobalt / activity) indicate the acid values (mg-KOH/g) of oxidation products obtained as a result of reacting a reaction solution (2.0 g of *p*-toluic acid, 0.3 g¹ of paraldehyde, 0.003 g of cobalt acetate tetrahydrate, and 8 g of acetic acid containing 1% water) for four hours at 110°C and at an oxygen partial pressure of 20 kg/cm² (gauge pressure). Similarly, the color tone (T%) of the terephthalic acid after slurry washing has been performed is the transmittance of a solution consisting of 5 g of sample dissolved in 50 mL of a 10% aqueous solution of sodium hydroxide as measured at a wavelength of 400 mμ, a slit width of 1.0 mμ, and a cell length of 10 mm. The purity of the purified terephthalic acid was measured with the help of gas chromatography after dimethyl ester conversion.

Working Examples 1 to 6

8.6 parts of *p*-xylene, 3 parts of paraldehyde, and 2.6 parts of acetic acid containing 2% water and 1.4% cobalt acetate were introduced per hour into a reaction vessel equipped with a multi-tube type heat exchanger. Separately, air was introduced from the bottom of the reaction vessel at 35 Nm³ per hour, and an oxidation reaction of *p*-xylene was performed while a 40 atm pressure, a 130°C temperature, and a 4.0 hour retention time were maintained. The reaction mixture was continuously collected from the reaction vessel, and the crude terephthalic acid cake and reaction mother liquor were centrifugally separated. As the first low-temperature wash, 1.5 parts of crude terephthalic acid cake (containing 1 part of terephthalic acid) and 4 parts of acetic acid containing 20% water that had been recovered were mixed in a stainless steel vessel, and the mixture was stirred for 45 minutes at 100°C. The slurry was cooled to 70°C and

¹ Translator's note: Appears to be a typographical error for "0.3 g."

centrifuged, resulting in the first-stage wash terephthalic acid cake. The acetic acid was recovered as a result of evaporating the separated first-stage wash mother liquor, and was re-used for the first stage wash. Meanwhile, the cobalt acetate recovered from the first-stage wash mother liquor contained in the bottom waste was returned to the reaction vessel and re-used for *p*-xylene oxidation.

As the second wash, 1.5 parts of terephthalic acid cake from the first wash (containing one part of terephthalic acid) and 4 parts of recovered acetic acid having a 20% water content were mixed in a stainless steel vessel, and the mixture was stirred for 90 minutes at 160°C in a slurried state. The slurry was cooled to 110°C, and then centrifugally separated into purified terephthalic acid cake and wash mother liquor. The purified terephthalic acid cake was dried and supplied for the manufacture of polyethylene terephthalate. Meanwhile, the wash mother solution was evaporated off to recover the acetic acid, which was re-used for washing.

The following table shows the activity of cobalt acetate recovered from the first wash solution as an oxidation catalyst and the purity and color tone of the purified terephthalic acid when only the treatment temperature in the first stage wash and the treatment temperature in the second stage wash were changed.

Working Example No.	Heating temperature (°C)		Activity of recovered cobalt in first stage wash	Characteristics of purified terephthalic acid	
	First-stage wash	Second-stage wash		Purity (%)	Color tone (T%)
1	100	160	655	99.8	94.8
2	50	160	650	99.6	95.2
3	125	160	648	99.8	96.0
4	100	145	655	99.5	93.0
5	100	155	655	99.6	94.5
6	100	175	655	99.7	92.8

Comparative Examples 1 to 6

The following table shows the recovered cobalt activity and the characteristics of the purified terephthalic acid when the crude terephthalic acid cake was treated in the same manner as described in Working Example 1, except that the heating temperatures of the first stage wash and the second stage wash were beyond the range of the present invention.

Comparative Example No.	Heating temperature (°C)		Activity of recovered cobalt in first-stage wash	Characteristic values of purified terephthalic acid	
	First-stage wash	Second-stage wash		Purity (%)	Color tone (T%)
1	30	160	652	98.7	91.0
2	150	160	598	99.5	90.5
3	100	130	655	98.9	91.5
4	100	190	655	99.6	84.5
5	100	200	655	99.7	71.7
6	170	160	485	99.6	88.5

As is evident from Comparative Example 1, terephthalic acid having a purity of 99.0% or higher could not be obtained when the first stage wash was 30°C, which is below the level of the present invention, even when the second stage wash was set at 160°C, which is used in the present invention.

In contrast to Comparative Example 1, when the treatment temperature of the second stage wash in Comparative Example 3 was set to 130°C, which was below the level of the present invention, terephthalic acid of the target purity could not be obtained.

In Comparative Examples 2 and 6, when the first stage treatment temperature was set to 150°C, which exceeded the level of the present invention, the oxidation catalyst activity of the cobalt recovered from the first wash mother solution was greatly decreased.

In Comparative Examples 4 and 5, when the temperature of the first treatment was set to 100°C, which is the level used in the present invention, and the temperature of the second treatment was set to 190°C and 200°C, which were above the 180°C level used in the present invention, the color tone (T%) of the resulting terephthalic acid deteriorated considerably.

Working Examples 7 to 11

The following table shows the characteristics for purified terephthalic acid obtained under the same conditions as described in Working Example 1, except that different values were used for the water content of acetic acid used in the first and second slurry washes of the crude terephthalic acid cake.

Working Example No.	Water content of acetic acid (%)	Characteristics of purified terephthalic acid	
		Purity (%)	Color tone (T%)
7	5	99.6	93.5
8	10	99.7	95.0
9	20	99.8	94.8
10	30	99.6	94.2
11	40	99.5	93.0

Comparative Examples 7 to 10

The following table shows the characteristics for purified terephthalic acid obtained under the same conditions as described in Working Example 1, except that the water content of acetic acid used in the first and second slurry washes of the crude terephthalic acid cake was changed to levels beyond the range of the present invention.

Comparative Example No.	Water content of acetic acid (%)	Characteristics of purified terephthalic acid	
		Purity (%)	Color tone (T%)
7	1.0	99.2	87.0

8	90.0	99.3	88.5
9	70.0	99.8	88.2
10	100.0	98.9	85.5

When acetic acid had a water content exceeding the range of the present invention, a diminished purifying effect was obtained with regard to the crude terephthalic acid.

According to the present invention as described in the foregoing, cobalt compounds used in the air oxidation of *p*-dialkylbenzene can be quantitatively recovered with essentially no loss of catalytic activity. In addition, high-purity terephthalic acid can be simultaneously manufactured to levels hitherto unimaginable with conventional slurry washes.

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